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U1S S1645 S1783 S2003 S2013 S2029 S2193 S3035

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(58) continued overleaf

(54) Sliding member with film containing chromium and chromium nitride

(57) A wear- and seizure-resistant sliding member has chromium nitride film in which the chief phases or compositions are CrN and Cr<sub>2</sub>N. The sliding member is obtained by coating a substrate with a composite film of chromium nitride in which a metallic chromium structure is interspersed. The method of manufacturing the sliding member includes bringing a gaseous phase consisting of a mixture of chromium and nitrogen into contact with the substrate by the PVD method. Two targets 26 are used. The sliding member may be a piston ring or may be used in a cutting tool.

The wear resistance of the layer may be tested in a wear tester, as illustrated in fig 2, in which a test piece 5 is attached to a rotor 4 which is brought to bear against a polished disc 2. A pressing force is applied to the stator holder 1 so that the disc 2 and the pin-shaped projections 10 on the test piece 5 are brought into contact at a predetermined pressure and the rotor 4 is rotated. A rolling fatigue tester (fig 4, not illustrated) is also described.

FIG. 1

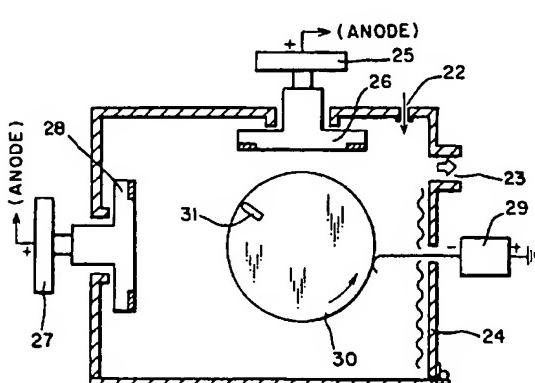
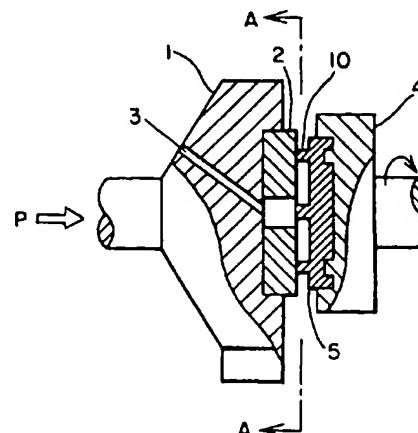


FIG. 2



GB 2 303 640 A

(58) Field of Search

UK CL (Edition O ) C7F FBAX FCSX FCVX FCXX FPCX

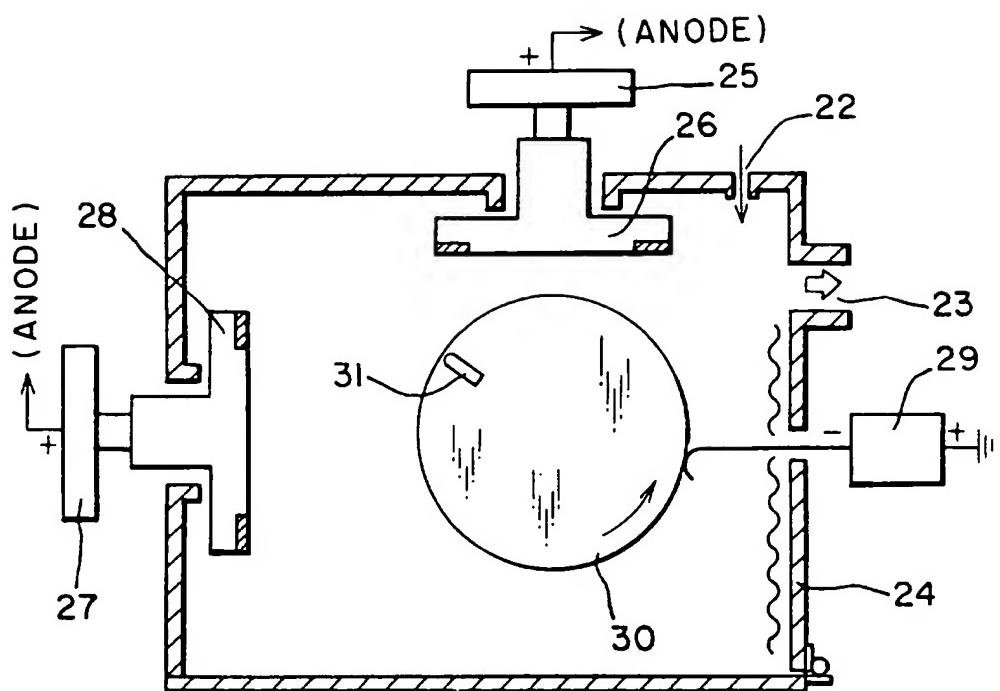
FPDX FPEX , F2A AD44 , F2T

INT CL<sup>6</sup> C23C 14/06 14/16 14/22 , F16C 33/12 , F16J 9/26

9/28

Online: WPI

FIG. I



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FIG. 2

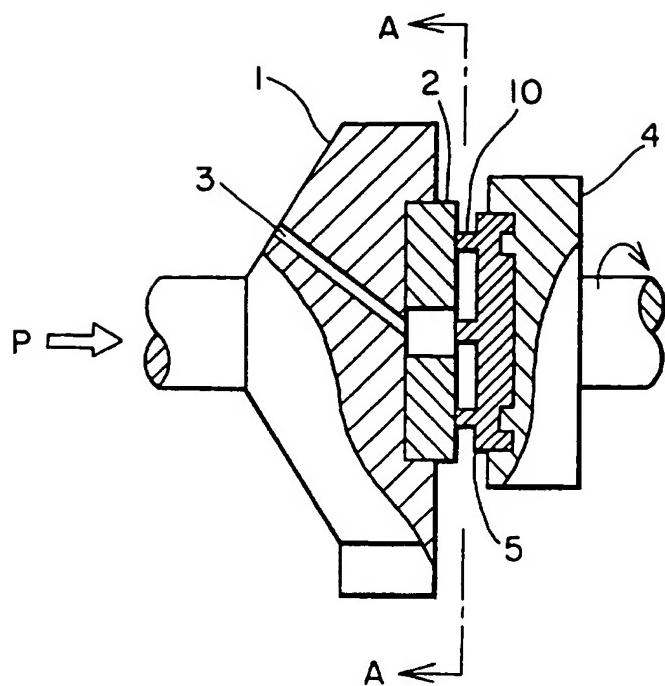
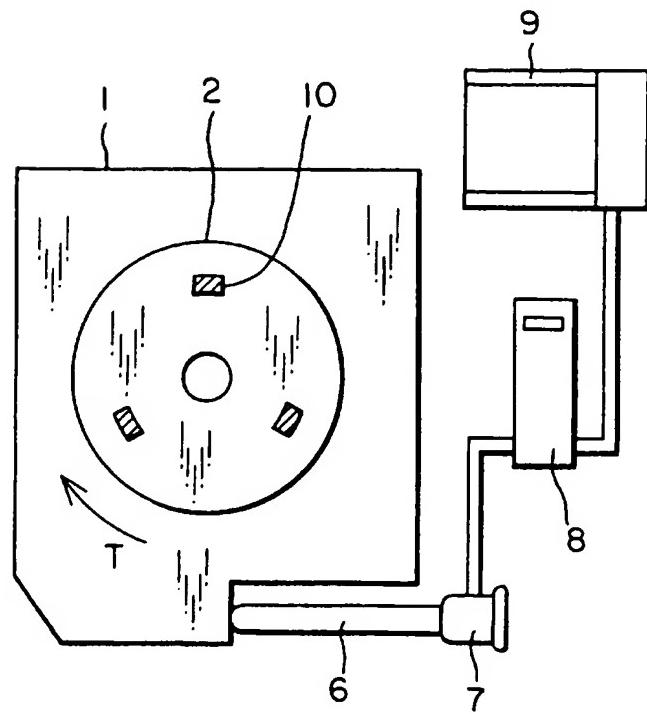
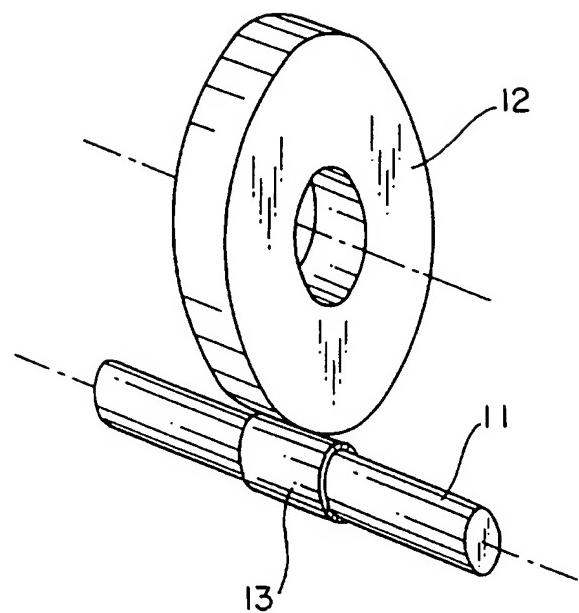


FIG. 3



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FIG. 4



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TITLE OF THE INVENTION

SLIDING MEMBER AND METHOD OF MANUFACTURING SAME

BACKGROUND OF THE INVENTION

5    Field of the invention

This invention relates to a sliding member exhibiting excellent abrasion resistance and excellent seizure resistance and having a film of chromium nitride in which CrN and Cr<sub>2</sub>N are the chief ingredients, as well as to a method of  
10 manufacturing this sliding member.

Description of the Prior Art

Sliding parts on which a film exhibiting excellent sliding characteristics is formed by a surface treatment find use where parts slide against each other, such as in automobile  
15 engine parts and the parts of various machines. Methods of surface treatment used heretofore include nitriding, chromium plating and molybdenum flame spraying.

The increasingly severe conditions under which sliding parts have come to be used in recent years has been  
20 accompanied by the demand for parts having improved sliding characteristics. Situations have arisen in which this demand can no longer be satisfied by conventional surface treatments, and hence there is greater need for films which exhibit outstanding abrasion and seizure resistance.

25       In an effort to satisfy these requirements, it has recently been proposed that the sliding surface of a sliding member be covered with a film of a metal nitride or metal

carbide by PVD (physical vapor deposition).

A PVD film such as titanium nitride (TiN), titanium carbide (TiC) and chromium nitride (CrN) exhibits excellent abrasion and seizure resistance. Among these, titanium  
5 nitride and chromium nitride in particular have become the focus of attention for use as practicable films, and such films are being used in some machine and engine parts.

However, conditions under which such parts are used are becoming increasingly harsh and the state of the art is  
10 such that even titanium nitride and chromium nitride are no longer considered to have satisfactory sliding characteristics. Particularly severe sliding conditions are encountered when sliding motion is accompanied by oscillatory motion normal to the sliding surface, thereby causing the  
15 surfaces of contact to separate, or when the load in the normal direction varies during sliding motion. Under harsh conditions such as these, hard films typified by a film of chromium nitride obtained by ion plating may chip and peel off, thereby shortening the service life of the sliding member.  
20 Similar chipping and peeling of hard films is observed even under severe lubrication conditions, as when it is difficult for a lubricating film to form on sliding portions because of elevated temperatures or increased contact load. Accordingly, there is demand for a sliding member covered with  
25 a ceramic coating film exhibiting chipping resistance and peeling resistance superior to that of the films obtained by conventional surface treatments.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a sliding member coated with chromium nitride film exhibiting both satisfactory seizure resistance and abrasion resistance, wherein the coating film will not chip or peel off even under severe conditions of use.

Another object of the invention is to provide a method of manufacturing such a sliding member.

The inventors have conducted exhaustive search with a view to resolve the aforementioned problems and have completed the present invention upon finding that a sliding member which exhibits excellent abrasion and seizure resistance and which will not readily chip or peel off is obtained by bringing a gaseous phase of mixed chromium and nitrogen into contact with a substrate by the PVD method to form a composite film, the chief phases of which are CrN and Cr<sub>2</sub>N and in which the metallic chromium structure is interspersed, on the surface of the substrate, at which time the size of the interspersed metallic chromium structure is adjusted to 0.2 ~ 5  $\mu\text{m}$  and the area ratio to 1 ~ 20%, which indicates the percentage of the total area of the film occupied by the metallic chromium structure.

More specifically, the sliding member of the present invention is characterized by the formation of a chromium nitride composite film the chief ingredients of which are CrN and Cr<sub>2</sub>N and in which the metallic chromium structure is

interspersed, with the size and area ratio of the metallic chromium structure being defined at the time of film formation.

Owing to the fact that the soft metallic chromium  
5 structure is uniformly interspersed in the film of chromium nitride, the film on the sliding member of the present invention has a tenacity which is superior to that of a film consisting of solely of chromium nitride having a high hardness.

10 In order to form the film in which the metallic chromium structure is interspersed in the chromium nitride structure, an ion plating method equipped with a plurality of sources is used for vaporization of metallic chromium. By adjusting the partial pressure of the reaction gas and making  
15 the distances between the workpiece to be treated at each of the metallic chromium vaporization sources, the speed of reaction between the vaporized chromium and reaction gas is controlled to form the objective film. By adjusting the partial pressure of the reaction nitrogen gas, the distances  
20 between the metallic chromium vaporization sources and the workpiece treated and the arc current ratio, it is possible to adjust the amount and size of the metallic chromium structure in the film as well as the composition of the chromium nitride.

25 The size of the metallic chromium structure is limited to 0.2 ~ 5  $\mu\text{m}$  and the area ratio thereof is limited to 1 ~ 20%. If the size of the metallic chromium structure is less

than  $0.2 \mu\text{m}$  or the area ratio is less than 1%, the effects of the metallic chromium structure are not particularly outstanding and no improvement in chipping resistance or peeling resistance is observed. Further, if the size of the  
5 metallic chromium structure is greater than  $5 \mu\text{m}$ , the metallic chromium structure becomes locally exposed at the surface and scuff resistance becomes inferior to that of the structure consisting of chromium nitride alone. If the area ratio is greater than 20%, film hardness declines and the  
10 resulting scuff resistance and abrasion resistance become inferior to those of the structure consisting of chromium nitride alone.

The overall thickness of the film is preferably 1 ~  
80  $\mu\text{m}$ , especially 20 ~ 60  $\mu\text{m}$ . If the film thickness is less  
15 than  $1 \mu\text{m}$ , the life of the film will be shortened by wear.  
If overall film thickness exceeds  $60 \mu\text{m}$ , on the other hand,  
the film will peel off or crack and adhesion to the substrate  
will decline. Making the film thicker than necessary is  
undesirable for reasons of economy.

20 Depending upon the particular application, the substrate coated with the film is selected from among iron materials, aluminum materials or titanium materials. The PVD method described in detail below is similar to treatments of the type performed at temperatures lower than that used in  
25 methods such as CVD (chemical vapor deposition). However, since heat input due to the vaporization phenomenon is unavoidable, it is preferred that heat-resistant iron or

titanium material be adopted as the substrate if possible.

The foregoing relates to a method of forming a chromium nitride film having an interspersed metallic chromium structure on a substrate. However, according to the invention,  
5 it is also permissible to interpose a primary coat of metal between the film and the substrate. If ion plating is carried out before the introduction of the nitrogen gas during the process for forming the film described above, a primary coat of chromium metal will be formed on the substrate. Since the  
10 primary coat of chromium metal has a thermal coefficient of expansion near that of the substrate and is not susceptible to the effects of thermal stress, the primary coat exhibits excellent adhesion and flexibility. It is preferred that the primary coat of chromium metal be formed to a thickness of  
15 0.1 ~ 2  $\mu$  m. A primary coat having a thickness of less than 0.1  $\mu$  m will not manifest much improvement in adhesion. Increasing the thickness beyond 2  $\mu$  m does not provide a commensurate improvement in adhesion and is disadvantageous economically.

20 Forming a primary coat excelling in adhesion and flexibility between the film and the substrate in the manner described has the effect of preventing peeling of the film.

Other features and advantages of the present invention will be apparent from the following description  
25 taken in conjunction with the accompanying drawings, in which like reference characters designate the same or similar parts throughout the figures thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view illustrating the set-up of an ion plating apparatus;

5 Fig. 2 is a side view, partially broken away, illustrating an ultra-high-pressure wear tester;

Fig. 3 is a sectional view taken along line A-A of Fig. 2; and

10 Fig. 4 is a perspective view for describing the essentials of a rolling fatigue tester.

DESCRIPTION OF THE PREFERRED EMBODIMENT

A specific embodiment of the invention will now be described in detail.

15 According to the present invention, a mixture of chromium and nitrogen in the gaseous phase is brought into contact with a substrate by the PVD method. The PVD method is one technique for forming a film and basically can be classified into three processes, namely vapor deposition, 20 sputtering and ion plating.

In the present invention, the process most preferred is reactive ion plating, in which chromium vapor is reacted with nitrogen to deposit a film of chromium nitride on the substrate.

25 The chromium vapor is obtained by irradiating chromium with a high-energy beam such as an electron beam from an HCD gun in order to vaporize the chromium. Chromium vapor

may also be obtained by emitting chromium particles from a cathode, as is performed in anodic arc-plasma ion plating or sputtering.

When a plasma is produced in a gaseous phase in which  
5 nitrogen has been mixed with chromium vapor, the chromium is  
ionized and forms bonds with the nitride ions to produce  
chromium nitride. As a result, a film of chromium nitride is  
formed on the surface of the substrate. Though the invention  
will be described below taking the ion plating process as an  
10 example, the invention is not limited to use of the ion plating  
process.

Fig. 1 illustrates an example of an ion plating  
apparatus used in the present invention. The apparatus  
includes a vacuum vessel 24 having an inlet 22 for nitrogen  
15 gas and an exhaust port 23. A first target 26 connected to  
the cathode of an arc power supply 25 and a second target 28  
connected to the cathode of an arc power supply 27 are placed  
inside the vacuum vessel 24. Metallic chromium has been set  
on the first and second targets, which are disposed so as to  
20 have different distances from a workpiece 31 to be treated.  
Also placed within the vacuum vessel 24 is a rotary table 30  
connected to a bias supply 29. The workpiece 31 is placed on  
the rotary table 30.

A method of forming the film of the present invention  
25 on the workpiece 31 using this ion plating apparatus will now  
be described.

First, the workpiece 31 is cleaned to remove

contaminants attached to the surface thereof, the workpiece is allowed to dry sufficiently and is then inserted into the vacuum vessel 24 of the ion plating apparatus. The vessel 24 is then evacuated from the exhaust port 23. After the vessel  
5 is evacuated to such an extent that the pressure inside the vessel attains a value of  $1.3 \times 10^{-3} \sim 5 \times 10^{-3}$  Pa, the vessel is heated by a heater incorporated in the ion plating apparatus, whereby the substrate is caused to give off its inherent gas.

A heating temperature of 300 ~ 500°C is preferred.

10 At the moment the pressure inside the vessel falls below  $4 \times 10^{-3}$  Pa, the chromium targets are used as cathodes and an arc discharge is produced at the surface thereof to produce an emission of chromium. At this time a bias voltage is impressed upon the workpiece 31 so that the metal ions  
15 emitted from the cathodes bombard the substrate surface at a high energy. This method is so-called "bombard cleaning" by which oxides are removed from the substrate surface and the surface is subjected to an activation treatment. The bias voltage applied at this time is preferably -700 ~ -900 V.

20 Thereafter, the bias voltage is lowered and chromium ions are deposited on the substrate surface, during which time nitrogen gas is introduced into the vessel and is passed through the plasma to ionize nitrogen. At this time the partial pressure of nitrogen is made  $1.3 \times 10^{-1} \sim 13.3$  Pa and  
25 a bias voltage of 0 ~ -100 V is applied to form an ion plating film on the surface of the substrate.

When the film is formed, the vaporized chromium

particles from the first target 26 collide with the nitrogen molecules of the reaction gas at a comparatively low probability since the first target 26 has a short distance from the workpiece 31. For the same reason, the nitrogen 5 molecules have a short transit time through the plasma. As a consequence, ionization does not readily take place and the metal can be deposited on the workpiece 31 by suitably selecting the gas partial pressure and the aforementioned distance. Since the distance between the second target 28 and 10 the workpiece 31 is greater than that between the first target 26 and the workpiece 31, the vaporized chromium particles from the second target 38 are capable of forming a deposit of Cr<sub>2</sub>N, a deposit of a film which is a mixture of Cr<sub>2</sub>N and CrN, or a deposit of CrN, depending upon the selection of the partial 15 pressure of the gas and the distance to the workpiece 31. In other words, by suitably selecting the partial pressure of the gas, placing the first target 26 at such a distance that metallic chromium is deposited and placing the second target at such a distance that chromium nitride is deposited, it is 20 possible to form a film having a mixed composition consisting of metallic chromium and chromium nitride.

Further, by suitably setting the values of the arc currents passed through the individual targets and the distances between the targets and the workpiece, it is 25 possible to change the ratio of the composite of the metallic chromium structure and chromium nitride structure and to control the size and area ratio of the interspersed metallic

chromium structure.

The actions and effects of the invention will now be described based on a specific embodiment.

Various composite films of chromium nitride having an interspersed metallic chromium structure were formed on the surface of a test piece of SUS 440 by the method described above.

The distance between the first target and the workpiece was set at about 50 mm, it having been confirmed from the results of preliminary experiments that this distance would deposit metallic chromium. It was also verified that the size of the metallic chromium structure is proportional to the arc current. The area ratio of the metallic chromium structure can be adjusted by setting the ratio between the two arc current values.

Furthermore, the distance between the second target and the workpiece was made about 200 mm. The composition differs depending upon the partial pressure of nitrogen. Specifically, Cr<sub>2</sub>N, the film of the Cr<sub>2</sub>N + CrN mixture and CrN change as the partial pressure of nitrogen rises.

The composition of each film was measured by X-ray diffraction, the size and area ratio of the metallic chromium structure were measured by EPMA and the hardness of the film was measured by a micro-Vickers hardness tester. Table 1 illustrates the conditions under which the specimens according to the invention were produced as well as the results of measurement.

TABLE 1

| COATING CONDITION   | EXAMPLE 1             | EXAMPLE 2                  | EXAMPLE 3 | EXAMPLE 4 | EXAMPLE 5 | EXAMPLE 6 |
|---|-----------------------|----------------------------|-----------|-----------|-----------|-----------|
| DISTANCE BETWEEN FIRST TARGET AND WORKPIECE (mm)            | 50                    | 50                         | 50        | 50        | 50        | 50        |
| FIRST TARGET ARC CURRENT (A)                                | 100                   | 100                        | 100       | 90        | 140       | 140       |
| DISTANCE BETWEEN SECOND TARGET AND WORKPIECE (mm)           | 200                   | 200                        | 200       | 200       | 200       | 200       |
| SECOND TARGET ARC CURRENT (A)                               | 200                   | 200                        | 200       | 200       | 200       | 150       |
| NITROGEN PARTIAL PRESSURE(Pa)                               | 0.5                   | 0.7                        | 1.0       | 1.0       | 1.0       | 1.0       |
| COATING TIME (min)  | 120                   | 120                        | 120       | 120       | 120       | 120       |
| RESULTS OF MEASUREMENT                                      |                       |                            |           |           |           |           |
| COMPOSITION   | Cr, Cr <sub>2</sub> N | Cr, Cr <sub>2</sub> N, CrN | Cr, CrN   | Cr, CrN   | Cr, CrN   | Cr, CrN   |
| HARDNESS  | 1400~1900             | 1400~1900                  | 1400~1900 | 1400~1900 | 1400~1900 | 1200~1700 |
| FILM THICKNESS $\mu\text{m}$                                | 3.0                   | 2.9                        | 2.7       | 2.6       | 2.8       | 2.7       |
| AVERAGE DIAMETER OF METALLIC CHROME STRUCTURE $\mu\text{m}$ | 1.0                   | 1.1                        | 1.1       | 0.5       | 2.1       | 2.3       |
| AREA RATIO OF METALLIC CHROME STRUCTURE %                   | 7.1                   | 6.8                        | 5.9       | 2.8       | 7.4       | 8.6       |

To obtain comparative example, chromium nitride films well known in the art were produced and the properties thereof where measured in the manner described above (Comparative Examples 1 ~ 3). Comparative examples in which a metallic 5 chromium composition was interspersed in the chromium nitride film but in which the size and area ratio of the metallic chromium composition were inappropriate were also measured (Comparative Examples 4 ~ 6). Table 2 illustrates the conditions under which these control specimens were produced 10 as well as the results of measurement.

TABLE 2

| COATING CONDITION                                 |  | COMPARATIVE EXAMPLE 1 | COMPARATIVE EXAMPLE 2 | COMPARATIVE EXAMPLE 3 | COMPARATIVE EXAMPLE 4 | COMPARATIVE EXAMPLE 5 | COMPARATIVE EXAMPLE 6 |
|---|--|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| DISTANCE BETWEEN FIRST TARGET AND WORKPIECE (mm)  |  | 200                   | 200                   | 200                   | 50                    | 50                    | 50                    |
| FIRST TARGET ARC CURRENT (A)                      |  | 200                   | 200                   | 200                   | 70                    | 90                    | 200                   |
| DISTANCE BETWEEN SECOND TARGET AND WORKPIECE (mm) |  | 200                   | 200                   | 200                   | 200                   | 200                   | 200                   |
| SECOND TARGET ARC CURRENT (A)                     |  | 200                   | 200                   | 200                   | 220                   | 300                   | 100                   |
| NITROGEN PARTIAL PRESSURE(Pa)                     |  | 0.5                   | 0.7                   | 1.0                   | 1.0                   | 1.0                   | 1.0                   |
| COATING TIME (min)                                |  | 90                    | 90                    | 90                    | 120                   | 120                   | 120                   |
| RESULTS OF MEASUREMENT                            | COMPOSITION                                      | Cr <sub>2</sub> N     | Cr <sub>2</sub> N CrN | CrN                   | Cr, CrN               | Cr, CrN               | Cr, CrN               |
|   | HARDNESS   | 1700~2000             | 1700~2000             | 1700~2000             | 1500~1900             | 1500~1900             | 1100~1600             |
|   | film thickness μm                                | 2.8                   | 2.6                   | 2.5                   | 2.6                   | 3.5                   | 2.9                   |
|   | AVERAGE DIAMETER OF METALLIC CHROME STRUCTURE μm |                       |                       |                       | 0.1                   | 0.5                   | 5.7                   |
|   | AREA RATIO OF METALLIC CHROME STRUCTURE %        |                       |                       |                       | 0.5                   | 0.7                   | 21.4                  |

[Seizure Resistance]

The resistance of the material of the present invention to seizure was evaluated.

A test piece 5 consisting of SKD 61, JIS (corresponding 5 to ASTM, H-13, US Standard) was prepared. As shown in Figs. 2 and 3, the test piece 5 was provided with three pin-shaped projections 10, each having a length of 5 mm, a width of 5 mm and height of 5 mm, disposed equidistantly on the same circle. Test specimens were produced using this test piece 10 by forming the inventive film to a thickness of 20 ~ 30  $\mu$  m on the 5-mm square end face of each projection 10. A seizure-resistance test was conducted using an ultra-high-pressure wear tester. The test was conducted on the films of this embodiment and on the films of the comparative 15 examples formed by the method described above.

Furthermore, a similar test was performed using a test specimen obtained by forming a chromium plating film (Comparative Example 7) having a thickness of 100  $\mu$  m on the 5-mm square end face of a test piece.

20 The set-up of the ultra-high-pressure wear tester and the test conditions used in the test were as follows:

The test apparatus is illustrated diagrammatically in Fig. 2 and in Fig. 3, which is a sectional view taken along line A-A of Fig. 2. A polished disk 2 (the associated part 25 brought into frictional contact with the test specimens) having a diameter of 80 mm and a thickness of 10 mm is detachably mounted on a stator holder 1. Lubricating oil is introduced

to the center of the disk 2 from the side opposite the test piece 5 through a lubricating passageway 3. The arrangement is such that a pressing force  $P$  is applied to the stator holder 1 at a predetermined pressure from the right side by means 5 of a hydraulic device, not shown. A rotor 4 opposes the disk 2 and is rotated at a predetermined speed by a drive unit, not shown. The test piece 5 is attached to the rotor 4 in such a manner that the 5-mm square end faces of the projections 10 on which the surface-treatment layers have been formed are 10 free to slide against the disk 2 as sliding surfaces.

The predetermined pressing force  $P$  is applied to the stator holder 1 so that the disk 2 and the pin-shaped projections 10 on the test piece 5 are brought into contact at a predetermined surface pressure, and the rotor 4 is rotated 15 while the sliding surfaces are lubricated with oil supplied from the lubricating passageway 3 at a predetermined rate of lubrication. The pressure acting upon the stator holder 1 is increased in stages at fixed time intervals, and a torque  $T$  developed by the stator holder 1 owing to the friction between 20 the test piece 5 and the disk 2 brought about by rotating the rotor 4 is made to act upon a load cell 7 via a stainless steel fiber 6. Any change in torque  $T$  is read by a dynamic strain indicator 8 and recorded by a recorder 9. A sudden increase in torque  $T$  is construed to indicate the occurrence of seizure 25 and the acceptability of the seizure characteristic is judged based upon the contact surface pressure at such time. The material used for the disk 2 was iron, specifically FC 250,

JIS (ASTM class No. 4012, US Standard). The test conditions were as follows:

Friction Velocity: 8 m/sec

Disk material: FC 250

5 Contact surface pressure: After smoothing was performed at a surface pressure of 20 kgf/cm<sup>2</sup>, the pressure was raised at increments of 10 kgf/cm<sup>2</sup> until the occurrence of seizure. Each level of surface pressure was maintained  
10 for 3 min.

Lubricant: Motor oil #30

Temperature: 80°C

Supply rate: 250 cc/min

The results of measurement are illustrated in Table 3.

15

TABLE 3

|  | EXAMPLE<br>1 | EXAMPLE<br>2 | EXAMPLE<br>3 | EXAMPLE<br>4 | EXAMPLE<br>5 | EXAMPLE<br>6 | EXAMPLE<br>7 | COMPARATIVE<br>EXAMPLE<br>6 | COMPARATIVE<br>EXAMPLE<br>7 |
|--|--------------|--------------|--------------|--------------|--------------|--------------|--------------|-----------------------------|-----------------------------|
| VALUE AT WHICH<br>SEIZURE OCCURS<br>(kgf/cm <sup>2</sup> ) | 2 8 3        | 2 8 5        | 2 8 9        | 2 9 0        | 2 8 4        | 2 8 1        | 2 9 0        | 2 5 9                       | 2 5 3                       |

With the disk made of FC 250, the articles of the present invention experienced seizure at surface pressures of from 281 to 290 kgf/cm<sup>2</sup>. This is greater than the figure of 253 kgf/cm<sup>2</sup> for the chromium-plated article of the 5 comparative example and is equivalent to the figure for the film (Comparative Example 3) consisting solely of CrN, which exhibits excellent seizure resistance. Even if a metallic chromium structure is interspersed in the film of chromium nitride, the effects are minimal when the metallic chromium 10 structure is large and its area ratio is large (Comparative Example 6).

[Wear Resistance]

The material of the invention was subjected to a corrosion abrasion test by a Kaken-type wear tester. Test 15 pieces of substrate material consisting of SKD-6 were prepared. Each test piece had a length of 5 mm, a width of 5 mm and height of 20 mm, with one end being rounded to a curved surface having a radius R of 6 mm. These ends of the test pieces were coated with the films of the above-described embodiment and with the 20 films of the comparative examples to thicknesses of 20 ~ 35  $\mu$ m.

Furthermore, a similar test was performed using a test specimen obtained by forming a chromium plating film (Comparative Example 7) having a thickness of 100  $\mu$ m on the 25 rounded end of the above-mentioned test piece.

In the test, the surface-treated rounded end of the test specimen was abutted against the outer peripheral portion

of a drum-shaped associated part in such a manner that the curved surface of the drum-shaped associated part and the curved surface of the test specimen made linear contact, a predetermined load was applied and the drum-shaped associated  
5 part was rotated at a predetermined speed. Lubrication was carried out by dropping a fixed amount of an aqueous solution of sulfuric acid, adjusted to a pH of 2, on the contacting portions, thereby producing an acidic atmosphere. The test conditions were as follows:

10           Drum material: FC 250

Friction Velocity: 0.25 m/sec

Friction time: 6 hrs

Contact load: 4 kg

Atmosphere: An aqueous solution of sulfuric acid,  
15           adjusted to a pH of 2, allowed to drop on the sliding portions at a rate of 1.5 cc/min.

The results of measuring the amount of film abrasion are as shown in Table 4.

20

TABLE 4

|                               | EXAMPLE<br>1 | EXAMPLE<br>2 | EXAMPLE<br>3 | EXAMPLE<br>4 | EXAMPLE<br>5 | EXAMPLE<br>6 | EXAMPLE<br>7 | COMPARATIVE<br>EXAMPLE 6 | COMPARATIVE<br>EXAMPLE 7 |
|-------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------------------|--------------------------|
| AMOUNT OF<br>SPECIFIC<br>WEAR | 5. 7         | 5. 5         | 5. 1         | 4. 6         | 6. 2         | 6. 7         | 4. 1         | 22. 0                    | 100                      |

\* RELATIVE VALUES TAKING AMOUNT OF CHROME PLATING WEAR AS 100

The results are indicated by relative values taking the amount of wear of the chromium plating film as 100.

The articles according to the present invention reduce the amount of abrasion to from 1/20 to 1/25 of that of the chromium-plated articles of the comparative examples. The amount of abrasion exhibited by the articles of the present invention is equivalent to that of the film (Comparative Example 3) consisting solely of CrN, the wear resistance whereof is outstanding. Even if a metallic chromium structure is interspersed in the film of chromium nitride, the effects are minimal when the metallic chromium structure is large and its area ratio is large (Comparative Example 6).

[Peeling Resistance]

The peeling resistance of the film coated member according to the present invention was evaluated by a rolling fatigue tester (roller pitching tester) that employs slip. The substrate material of the test piece was a material obtained by carburizing SCM 420, JIS (chromium Molybdenum Steel) and had the shape of a roller having a diameter of 26 mm and a length of 28 mm. Films according to the invention and films according to the comparative examples were applied to the outer circumferential surface of such rollers to a thickness of about 50  $\mu$ m. The thicknesses of the various films were made uniform by adjusting coating time.

The set-up of the pitching tester and the test conditions used in the test were as follows:

The test apparatus is illustrated diagrammatically in

Fig. 4. The apparatus includes a test roller 11 to which a test piece 13 having a diameter of 26 mm and a length of 28 mm is attached, and a load roller 12 arranged to oppose the test roller 11. It is so arranged that a pressing force is applied at a predetermined pressure. The test roller 11 is rotated at a predetermined speed by a drive unit, not shown. A surface-treatment layer is formed on the outer circumferential surface of the test piece 13. The load roller 12 has a diameter of 130 mm and a length of 18 mm, and the outer circumferential portion thereof is rounded to a radius of 300 mm so that the load roller 12 and test piece 13 come into point contact when viewed microscopically. The arrangement is such that a large pressing force is applied. Further, the load roller 12 follows up the test roller 11 via gears (not shown) and rotates while slipping relative to the test roller 11. The slip factor is represented by  $(U_{13}-U_{12})/U_{13}$ , where  $U_{13}$  represents the peripheral speed of the test piece and  $U_{12}$  the peripheral speed of the load roller. The slip factor can be selected at will. Lubricating oil is introduced into the contacting portions of the load roller 12 and test piece 13 through a lubricating passageway, which is not shown.

A predetermined pressing force is applied to the test piece 13 so that the test piece 13 and contact roller 12 are brought into contact at a predetermined surface pressure, the load roller 12 is rotated while the contacting portions are lubricated with oil supplied at a predetermined rate of

lubrication, and the load roller 12 is rotated at a predetermined slip factor.

The surface of the test piece was observed very carefully periodically during testing, and the acceptability 5 of peeling resistance was judged from the sum total of revolutions up to the occurrence of chipping-type peeling at the surface of the test piece. The load roller 12 serving as the associated part was made of FC 250. The test conditions were as follows:

10           Surface pressure (hertz stress): 160 kgf/mm<sup>2</sup>

Peripheral speed of test piece: 82 m/s

Slip factor: 20%

Oil used: #30 (base oil)

Oil flow rate: 1200 cc/min

15           Oil temperature: 80°C

The results of measurement are illustrated in Table 5.

TABLE 5

|          | EXAMPLE<br>1    | EXAMPLE<br>2    | EXAMPLE<br>3    | EXAMPLE<br>4    | EXAMPLE<br>5    | EXAMPLE<br>6    | COMPARATIVE<br>EXAMPLE 1 | COMPARATIVE<br>EXAMPLE 2 | COMPARATIVE<br>EXAMPLE 3 | COMPARATIVE<br>EXAMPLE 4 | COMPARATIVE<br>EXAMPLE 5 |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| NUMBER   | NO              | NO              | NO              | NO              | NO              | NO              | PEELING                  | PEELING                  | PEELING                  | PEELING                  | PEELING                  |
| OF TIMES | OCCURRENCE      | OCCURRENCE      | OCCURRENCE      | OCCURRENCE      | OCCURRENCE      | OCCURRENCE      | AFTER                    | AFTER                    | AFTER                    | AFTER                    | AFTER                    |
| AT WHICH | AFTER           | AFTER           | AFTER           | AFTER           | AFTER           | AFTER           | $3.1 \times 10^4$        | $3.2 \times 10^4$        | $2.9 \times 10^4$        | $4.6 \times 10^4$        | $5.6 \times 10^4$        |
| PEELING  | $2 \times 10^7$ | TIMES                    | TIMES                    | TIMES                    | TIMES                    | TIMES                    |
| OCCURS   | TIMES           | TIMES           | TIMES           | TIMES           | TIMES           | TIMES           |                          |                          |                          |                          |                          |

The articles produced in accordance with the invention exhibit a peeling resistance that is far superior to that of the hard chromium nitride of the comparative examples. Comparative examples 4 and 5 indicate that even if 5 the metallic chromium structure is interspersed in the film of chromium nitride, peeling tends to occur if the structure size is too small or the surface ratio too low.

Thus, as described above, the present invention provides a sliding member which is superior to the 10 conventionally used hard films in terms of wear and seizure resistance, and in which chipping and peeling do not readily occur, by forming a composite film on the surface of a substrate by the PVD method, wherein the chief phases or compositions of the film are CrN and Cr<sub>2</sub>N and contains an 15 interspersed metallic chromium structure. The invention further provides a method of manufacturing the sliding member.

The sliding member provided by the invention is well suited for use in sliding parts, examples of which are engine parts such as piston rings and cam followers, and compressor 20 parts such as shoe disks. The sliding member also finds use in various cutting tools.

As many apparently widely different embodiments of the present invention can be made without departing from the spirit and scope thereof, it is to be understood that the 25 invention is not limited to the specific embodiments thereof except as defined in the appended claims.

CLAIMS:

1. A sliding member comprising a film having a composite structure the chief phases or compositions of which are metallic chromium and chromium nitride, and a substrate coated 5 with said film, said metallic chromium being interspersed in said film and having a structure exhibiting a size of 0.2 to 5  $\mu$ m.
2. The sliding member according to claim 1, wherein said 10 chromium nitride in said film has a structure comprising a chemical composition consisting of CrN or Cr<sub>2</sub>N or a mixture thereof.
3. The sliding member according to claim 1 or 2, wherein 15 a primary layer comprising chromium is interposed between said film and said substrate.
4. The sliding member according to any one of claims 1 through 3, wherein said sliding member is a piston ring.  
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5. A sliding member coated with a composite film of chromium nitride in which a metallic chromium structure is interspersed, wherein said interspersed metallic chromium structure exhibits an area ratio, which indicates percentage 25 of the total area of said film occupied by said metallic chromium structure, of 1 to 20%.

6. The sliding member according to claim 5, wherein said chromium nitride in said film has a structure comprising a chemical composition consisting of CrN or Cr<sub>2</sub>N or a mixture thereof.

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7. The sliding member according to claim 5 or 6, wherein a primary layer comprising chromium is interposed between said film and said substrate.

10 8. The sliding member according to any one of claims 5 through 7, wherein said sliding member is a piston ring.

9. A method of manufacturing the sliding member described in any one of claims 1 through 8, comprising a step  
15 of bringing a gaseous phase consisting of a mixture of chromium and nitrogen into contact with a substrate by a physical vapor deposition method, thereby forming said film on said substrate.



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Application No: GB 9615539.5  
Claims searched: 1-9

Examiner: Peter Beddoe  
Date of search: 10 October 1996

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C7F (FPCX, FPDX, FPEX, FCSX, FCVX, FCXX, FBAX); F2A AD44  
F2T

Int Cl (Ed.6): C23C (14/06, 14/16, 14/22); F16C 33/12; F16J (9/26, 9/28)

Other: Online: WPI

**Documents considered to be relevant:**

| Category | Identity of document and relevant passage                              | Relevant to claims |
|----------|--|--------------------|
| X        | GB 2296504 A (NIPPON) see embodiment 5 (p19) & embodiments 20,21 (p27) | 1,5,9              |
| X        | GB 2296257 A (TEIKOKU) see esp table 1 at p10                          | 1,5,9              |
| X        | GB 2294950 A (KABUSHIKI) see sample D in Table 1 at p17                | 1,5,9              |
| X        | GB 2243162 A (KABUSHIKI) see specimens A,B at p11                      | 1,5,9              |
| X        | US 5205188 (REPENNING) see esp col 2 lines 34-51                       | 1,5,9              |
| X        | WPI Accession no 95-191040/25 & JP 7109561 A (NISSHIN) see abstract    | 1,5,9              |
| X        | WPI Accession no 95-041688/06 & JP 6322515 A (RIKEN) see abstract      | 1,5,9              |
| X        | WPI Accession no 93-318064/40 & JP 5231543 A (HINO) see abstract       | 1,5,9              |
| X        | WPI Accession no 91-263193/36 & JP 3172504 A (RIKEN) see abstract      | 1,5,9              |
| X        | WPI Accession no 87-323508/46 & JP 62228648 A (RIKEN) see abstract     | 1,5,9              |

|   |   |   |  |
|---|---|---|--|
| X | Document indicating lack of novelty or inventive step   | A | Document indicating technological background and/or state of the art.  |
| Y | Document indicating lack of inventive step if combined with one or more other documents of same category. | P | Document published on or after the declared priority date but before the filing date of this invention.          |
| & | Member of the same patent family  | E | Patent document published on or after, but with priority date earlier than, the filing date of this application. |



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|----------|--|--------------------|
| X        | WPI Accession no 87-189853/27 & JP 62120471 A (RIKEN) see abstract   | 1,5,9              |
| X        | Thin Solid Films, vol 185, pages 219-230, 1990 article entitled "The morphology ... ion reactive ion plating" by D Wang & T Oki, see esp pages 222 & 223 | 1,5,9              |

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| Y Document indicating lack of inventive step if combined with one or more other documents of same category. | P Document published on or after the declared priority date but before the filing date of this invention.          |
| & Member of the same patent family  | E Patent document published on or after, but with priority date earlier than, the filing date of this application. |